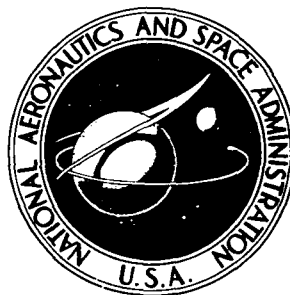


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**POLYMERIC MEMBRANE SYSTEMS
OF POTENTIAL USE FOR
BATTERY SEPARATORS**

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16. Abstract Two membrane systems were investigated that may have potential use as alkaline battery separators. One system comprises two miscible polymers: a support polymer (e. g. , polyvinyl formal) and an ion conductor such as polyacrylic acid. The other system involves a film composed of two immiscible polymers: a conducting polymer (e. g. , calcium polyacrylate) suspended in an inert polymer support matrix, polyphenylene oxide. Resistivities in 45-percent potassium hydroxide and qualitative mechanical properties are presented for films comprising various proportions of conducting and support polymers. In terms of these parameters, the results are encouraging for optimum ratios of conducting to support polymers.					
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POLYMERIC MEMBRANE SYSTEMS OF POTENTIAL USE FOR BATTERY SEPARATORS

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SUMMARY

Two membrane systems were investigated that may have potential use as alkaline battery separators. The first system comprises two miscible polymers: a support polymer (e. g. , polyvinyl formal) and an ion conductor (polyacrylic acid or polymethacrylic acid). Best results in terms of good mechanical strength and high conductivity in 45-percent aqueous potassium hydroxide (KOH) were observed for a membrane prepared from polyvinyl alcohol and polyacrylic acid in the ratio 2:1 and treated with formaldehyde. Other less promising aldehyde derivatives investigated included those made from glyoxal, glutaraldehyde, butyraldehyde, p-hydroxy benzaldehyde, and terephthalaldehyde.

The second system involved a film composed of two immiscible polymers: a conducting polymer suspended in an inert nonconducting polymer support matrix. The particular systems discussed in this report are the conducting polymers calcium polyacrylate and radiation-cross-linked polyacrylic acid suspended in the inert polymer polyphenylene oxide (PPO). Good flexibility and high conductivity in 45-percent aqueous KOH were found for calcium polyacrylate - PPO films. Mechanical and conducting properties of films containing cross-linked polyacrylic acid were generally inferior to those of films made from calcium polyacrylate.

INTRODUCTION

Recent interest in high-energy-density rechargeable batteries has led to extensive research on separators, particularly for alkaline cells. The importance of a good battery separator arises primarily from the need for long cycle life. Separators to date fall into two broad categories, namely, those in which conducting ions pass through molecular-size channels and those with a physically porous structure. The former category is represented by films or membranes composed of certain hydrophylic organic

polymers. These include cellulose and polyvinyl alcohol as well as more recent innovations involving ion exchange resins, graft polymers, and copolymers. Separators of the second type are cups, plates, and films that are physically porous such as porous porcelain cups, compacted refractory oxide plates, and the inorganic-organic Astropower-type separators for alkaline cells under development at the Lewis Research Center.

In this report, an investigation of two ion-conducting membrane systems is discussed. The first system falls into the molecular-size-channel category. The membrane explored was a solid solution of two polymers: a polyvinyl acetal to provide strength and support and a simple polyacid for ion conduction. The second system was a microporous film composed of two immiscible materials: an ion-conducting polymer, calcium polyacrylate or cross-linked polyacrylic acid, suspended in the polymer support matrix, polyphenylene oxide (PPO). In some respects this separator is similar to the inorganic-organic Astropower separator in use by NASA for the silver-zinc (Ag-Zn) battery.

Previous workers in search of better separator materials have been mainly concerned with organic polymers. These have ranged from regenerated cellulose to complex synthetic materials.

The use of cellulose as a separator was a forward step which made the Ag-Zn secondary battery practical (ref. 1, p. 263). Unfortunately, cellulose films suffered significant degradation as a result of reaction with battery constituents. Polyvinyl alcohol films were also attacked by alkaline silver oxide, but not as extensively as cellulose (ref. 2). Three other types of polymeric membrane separators subsequently investigated were grafted polymers, copolymers, and inorganic-organic composites.

For grafted polymeric membranes, a nonconducting but stable base resin film such as polyethylene or polypropylene is first prepared. This film may then be chemically modified by grafting with an ionic conducting species such as an organic acid to yield a membrane of good ionic conductivity in alkaline electrolyte. An example is the grafted polymer of polyethylene and acrylic acid, which is composed of the polyethylene backbone with side chains containing carboxylic acid groups. Grafted polymers may be further modified by cross-linking. A good conducting film in concentrated potassium hydroxide (KOH) electrolyte was formed by grafting vinyl acetate on polyethylene and subsequently hydrolyzing the vinyl acetate to produce a grafted polyalcohol chain (ref. 1, p. 273). Both radiation and chemically grafted polyethylene looked promising in short-term tests in Ag-Zn batteries (ref. 2); however, in longer tests (ref. 3) cross-linked polyethylene grafted with acrylic acid was attacked by the oxidative caustic environment, which caused degrafting with corresponding loss in conductivity. Another disadvantage of these grafted polymers was their tendency to be nonuniform in composition.

Various copolymers and terpolymers with active carboxylic groups have been investigated as battery separator materials. The active substituent may be acrylic acid, methacrylic acid, or maleic anhydride. Development of such materials began with

ethylene - acrylic acid copolymers. Because ethylene and acrylic acid do not copolymerize readily, a precursor copolymer of ethylene and methyl acrylate was prepared and subsequently hydrolyzed in aqueous KOH (ref. 4). Films of this material had good conductivity at high acrylic acid content and were stable in hot 40-percent KOH (140° C for 60 hr). Although tensile strengths were not high, they were adequate for normal handling.

The copolymers may also contain ligand groups. Two types of ligand-containing polymers developed for Ag-Zn batteries were the modified styrene - maleic anhydride - methyl methacrylate - methyl acrylate tetrapolymer and the modified 2-vinyl pyridine - methyl acrylate copolymer (ref. 5). The solubility of the tetrapolymer in aqueous 40-percent KOH was decreased by cross-linking with diamines. The resulting amide linkage was stable toward hydrolysis in hot 40-percent KOH. The second ligand-containing polymer-type (2-vinyl pyridine - methyl methacrylate copolymer) had a low ionic conductivity; conductivity was increased by hydrolysis of the methyl methacrylate during exposure to hot concentrated aqueous KOH. Of the ligand-type polymers tested, a 31:69 ratio, 2-vinyl pyridine - methyl methacrylate copolymer was selected (ref. 6) as the best potential separator material in terms of overall properties (e. g. , low resistivity and ease of handling during film preparation). The laboratory evaluation of ligand polymer films was favorable, which suggested that development on these systems should be undertaken to optimize chemical and physical properties so that they can be used as separators in alkaline batteries.

Recent trends in NASA separator development for Ag-Zn batteries are toward inorganic-organic separators. The Astropower separator was the first of this type (ref. 7) and was evaluated at the Lewis Research Center (ref. 8). Such a separator which has been successful in Ag-Zn cells is a microporous separator in which various inorganic compounds are bound in an inert polymer matrix. For example, a separator of this type may be made by coating pretreated asbestos sheet with a slurry composed of calcia-stabilized zirconium dioxide and pigmentary potassium titanate (PKT) suspended in a chloroform solution of PPO and a low-molecular-weight polyester, Plastolein P-9750. A detailed procedure for slurry preparation and coating has been given by Sheibley (ref. 9). The conduction mechanism is believed to involve microporous channels that form between the inorganic filler particles and the inert polymer (ref. 10). Inert support polymers other than PPO may also be used in inorganic-organic separators; in fact, a low-cost separator developed at the Lewis Research Center giving high cycle life in nickel-zinc (Ni-Zn) batteries makes use of synthetic rubber in place of PPO (ref. 11).

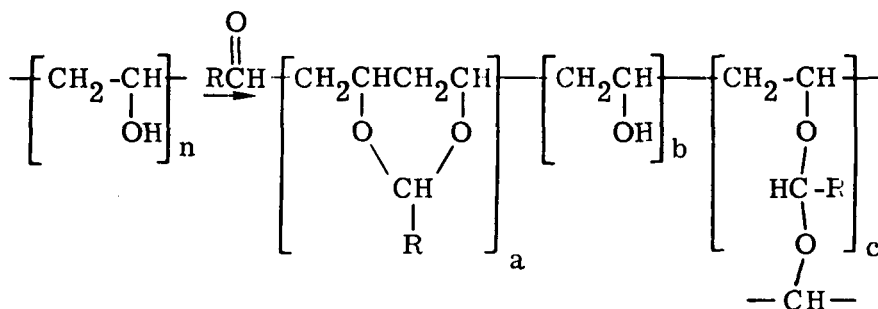
In spite of a great effort in battery separator development, present separators fall short of ideal with respect to long cell cycle life, high conductivity, and low cost; thus, research for better separators is continuing. The work described in this report is an investigation of new types of membranes that might be useful as separator materials. In

accord with our interest in alkaline Ag-Zn and Ni-Zn batteries, the research was directed to films which would be useful in concentrated aqueous KOH electrolyte; thus, our concern centered around good conductivity, chemical inertness, and good mechanical properties of membranes in this electrolyte. Other factors such as ease of fabrication and cost were also considered.

EXPERIMENTAL PROCEDURE

Solid-Solution Membranes (Homogeneous Polyblends)

The membranes selected for the solid-solution category consisted of a polyvinyl acetal and a polyacid (polyacrylic acid or polymethacrylic acid). Because of the low solubility of polyacetals in the aqueous casting solution, the acetal had to be formed from polyvinyl alcohol in the already cast film. Polyvinyl alcohol reacts with aldehydes to form water-insoluble polyacetals (ref. 12):



Because the polyacetal was formed in situ on the already cast film, treated films probably had some unreacted hydroxyl groups. The extent of acetalization increases with the severity (time and temperature) of the aldehyde treatment. As the hydrophylic hydroxyl groups of the polyalcohol are used up in the acetalization reaction, the ionic resistance in the KOH electrolyte should increase. The use of the polyacid in the polymer was necessary to restore ionic conductivity.

A 10-percent polyvinyl alcohol solution was prepared by stirring 100-percent-hydrolyzed polyvinyl alcohol in warm water. When the polymer was dissolved, 25 milliliters of methanol was added for each 100 milliliters of aqueous polymer solution; stirring was continued until a homogeneous solution was obtained. A polyacid solution was then prepared by polymerizing a 10-percent-monomer solution in water by using a small amount of potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) as an initiator. The two solutions were mixed in the desired proportions.

The films were made by casting the polymer solution on a smooth glass plate by using a doctor blade. The films were allowed to dry over night at room temperature and then were easily removed from the glass. Each film was cut into 12- by 12-centimeter squares, which were placed, one at a time, in an aldehyde reagent in a 19-centimeter-diameter covered crystallizing dish. After treatment, the film squares were washed with water and treated with dilute aqueous sodium bicarbonate for at least 10 minutes to neutralize traces of acid. The films were again washed with water and air dried at room temperature. The dried film was cut into smaller test specimens (about 3 by 3 cm) and stored in 45-percent aqueous KOH.

Aldehyde Treatment Solutions

For formaldehyde, 50 grams of ammonium sulfate and 3 milliliters of concentrated sulfuric acid were dissolved in 100 milliliters of water. Then, 100 milliliters of 37-percent aqueous formaldehyde was added with stirring.

For glutaraldehyde, 20 grams of sodium sulfate, 25 milliliters of formic acid, and 100 milliliters of 25-percent aqueous glutaraldehyde were dissolved in 100 milliliters of water. For terephthalaldehyde, a solution of 2 milliliters of concentrated sulfuric acid in 20 milliliters of water was added to 100 milliliters of methanol and stirred. To this was added 20 grams of terephthalaldehyde, and the solution was stirred until all went into solution. Additional methanol may be added to facilitate complete dissolution of the terephthalaldehyde. For butyraldehyde and *p*-hydroxy benzaldehyde, the same formulation was used, with 20 milliliters of butyraldehyde and 20 grams of *p*-hydroxy benzaldehyde, respectively, replacing the terephthalaldehyde. For glyoxal, a solution was made comprising 100 milliliters of water, 3 milliliters of concentrated sulfuric acid, and 50 grams of ammonium sulfate; 100 milliliters of 40-percent aqueous glyoxal was then added to the solution.

Two-Phase Membranes (Heterogeneous Polyblends)

The preparation technique used for these membranes was similar to that used to make inorganic-organic films (ref. 10). To a solution of 40 grams of PPO in 30 milliliters of chloroform was added the specified amount of 1,2-propanediol; stirring was continued until all was in solution. The PPO solution was added to a ball mill together with the specified amount of filler, calcium polyacrylate or cross-linked polyacrylic acid. The mixture was milled for about 24 hours, and the resulting slurry was cast on glass to produce the film.

Preparation of Calcium Polyacrylate

A 10-percent solution of polyacrylic acid was made by polymerizing 10-percent aqueous acrylic acid by using a small amount of $K_2S_2O_8$ to initiate the reaction. (Polyacrylic acid may also be obtained commercially.) To the stirred solution of polyacrylic acid was added the stoichiometric amount of aqueous ammonia to form the ammonium salt. This solution was then added to a hot dilute calcium nitrate solution containing sufficient calcium nitrate to form calcium polyacrylate. The calcium polyacrylate precipitated as a doughlike material. The hot mixture containing the doughy precipitate was stirred for at least 1 hour with the doughlike mass being broken up with a heavy glass stirring rod. The clumps were removed from the supernatant liquid, broken into smaller clumps, and then dried at 100°C overnight. The dried pieces were then ball milled to a fine powder. Further purification to remove occluded ammonium salts was accomplished by stirring the finely divided milled material with a large volume of hot water. The polymeric calcium salt became doughlike again. This material was again dried as described previously and used in this condition for the preparation of the two-phase membranes.

Cross-Linked Polyacrylic Acid

A 5-percent aqueous solution of acrylic acid was placed in a flat crystallizing dish and irradiated with 2-MeV electrons at 5 microamperes from a linear accelerator (Dynamitron). After a radiation period of about 1/2 hour, cross-linked polyacrylic acid deposited as an insoluble crust on top of the liquid. The crust was removed, the supernatant liquid was again irradiated for about 1/2 hour, and the crust was removed again. This procedure was repeated until additional radiation produced no significant amounts of additional insoluble material. The separated deposited material was dried overnight at 100°C . The dried polymeric material was broken up as much as possible in a mortar and powdered in a ball mill. The cross-linked polymer was difficult to powder; thus, milling times were long, and milling had to be repeated after removal of powdered material from previous millings. The remaining lumps were from time to time broken up in a mortar. The material used was the milled fine powder.

Resistivity Measurements

The procedure and apparatus used in our direct-current resistance measurements are described in an Air Force Propulsion Laboratory publication on screening methods for battery separators (ref. 13).

RESULTS

Polyvinyl Acetal Films

The ionic resistivity of various polyvinyl acetal films is given in table I. As mentioned previously, these films had varying amounts of polyalcohol groups because the acetalization reaction was carried out on the polyvinyl alcohol in the already cast film. The number of alcohol groups should decrease with increasing time and temperature of treatment.

As the hydrophylic hydroxyl groups of the polyalcohol were used up in the acetalization reaction, the ionic resistivity in KOH electrolyte increased and became essentially nonconducting after prolonged treatment with aldehydes, as can be seen from table I. In many cases resistivity data for films of higher resistance were variable and not reproducible; however, these data suffice to indicate that highly acetalized films were poor ionic conductors in aqueous KOH.

The films with the best mechanical properties, such as toughness and strength, were polyvinyl alcohol films treated with formaldehyde. The films treated with the other aldehydes had inferior properties. The films treated with butyraldehyde and glyoxal were soft, whereas the derivatives of glutaraldehyde and terephthalaldehyde were hard and somewhat brittle. Films with good mechanical properties were obtained with p-hydroxybenzaldehyde, but they were still inferior to the formaldehyde films. With this taken into account, the films derived from the formaldehyde were further investigated.

Solid-Solution Films

Addition of a simple polymeric acid (polyacrylic acid or polymethacrylic acid) to the acetalized polyvinyl alcohol increased conductivity (table II); the conductivity in concentrated KOH electrolyte increased with increasing proportion of polyacrylic acid to polyvinyl formal. Unfortunately, the mechanical properties such as strength, especially wet strength, decreased with increasing proportion of polyacrylic acid. For example, films comprising equal weights of the two polymers after treatment with formaldehyde still had too low a wet strength for use as a practical battery separator. The optimum composition for the formaldehyde treated film in terms of low resistivity and good mechanical strength was a polyvinyl alcohol - polyacrylic acid weight ratio of about 2:1. On exposure to the KOH electrolyte, the polyvinyl formal - polyacrylic acid films increased in toughness and tensile strength in comparison with these same films when exposed to water. Using polymethacrylic acid instead of polyacrylic acid gave films of higher resistivity. These films were also less flexible than those containing polyacrylic acid.

Two-Phase Films

As mentioned previously, the second membrane system investigated can be considered to be a modification of the inorganic-organic separator developed at the Lewis Research Center in which a polymeric material is used instead of an inorganic material as the filler. Our membrane comprised a polymeric filler material (e. g. , calcium polyacrylate (CPA)) suspended in an inert nonconducting polymer (e. g. , PPO) containing a small quantity of an organic additive (e. g. , 1,2-propanediol). The presence of the additive was necessary for good ionic conductivity in KOH electrolyte (ref. 10). The resistivities in 45-percent KOH of membranes containing various proportions of these three components are listed in table III. The higher the polymeric filler content of the film, the lower the resistivity; but, increasing the filler content also adversely affected mechanical properties, brittleness of the dry film especially. The fifth film composition listed in table III, which contained the highest filler content, was extremely brittle when dry and tore easily in concentrated KOH solution. The presence of more diol additive in the film made the film softer and decreased strength; at the same time, the resistivity dropped (table III). In general, the flexibility of these films was greater when they were submerged in 45-percent KOH than when dry. Good mechanical properties in aqueous KOH and low resistivities in this electrolyte were obtained from a film comprising PPO, CPA, and diol in the proportion 27:20:3. The flexible nature of these films in aqueous KOH was attributed to the tough gelatinous property of CPA when exposed to an aqueous environment.

Another polymeric filler material studied was radiation-cross-linked polyacrylic acid (PAA). The resistivities of films incorporating this filler material are given in table IV. The trends were similar to those for CPA in that increasing proportion of filler and diol led to lower resistivities at the expense of film strength. However, CPA had lower resistivity than PAA and also had better mechanical properties in that PAA made a soft film. Moreover, at high proportions of PAA, last composition listed in table IV, the films became mushy and consequently had poor wet strength in 45-percent KOH.

DISCUSSION

The first membrane type studied was a solid solution of two polymers, a water-soluble ion-conducting component in a water-insoluble polymer matrix. Because of the possibility that the water-soluble polymer in the film would gradually be leached by aqueous electrolytes and the film would be thereby weakened, such a membrane system should not be considered for use in many aqueous electrolytes. These membranes may be used, however, in certain electrolytes of high solute concentration, where polymer

solubility is substantially reduced by the salting-out effect. It is this effect that allows use of these membranes in concentrated aqueous KOH electrolytes.

We have investigated only several of the large number of polyacetals (determined by aldehyde used). Other aldehydes could be substituted for those used in our investigation; these would give other polymers, each with different melting point, stiffness, and solubility. As the conducting polymer in the matrix, two simple polyacids, polyacrylic acid and polymethacrylic acid, were examined; however, polymeric acids other than these two could also be used and could possibly give even better membrane properties. The number of combinations of matrix and conducting polymer is considerable, and these combinations would be subjects for further research.

In the present study of a small number of such combinations the best overall properties were obtained from a formaldehyde treated film of polyvinyl alcohol and polyacrylic acid in a 2:1 weight ratio. Although these films were somewhat delicate during the formaldehyde treatment, the air-dried films were tough and flexible. The membranes maintained their tough flexible properties even when immersed in 45-percent KOH. Apparently, the high KOH concentration inhibited dissolution of the film because of a salting-out effect. As expected, higher proportions of polyacrylic acid in the film led to increased ionic conductivity because this increase in polymeric acid content results in an increase in the concentration of carboxylic acid groups. Because of the water solubility of polyacrylic acid, films high in carboxylic acid content would also be expected to swell in KOH electrolyte. This swelling was observed, and it resulted in a decrease in mechanical strength.

Three dialdehydes were used in an attempt to make high-strength membranes with a cross-linked acetal structure. Membranes treated with glyoxal were soft and tacky, which suggested that little or no cross-linking took place in this case. Films treated with the dialdehyde glutaraldehyde were especially brittle when dry and had poor tear resistance in KOH electrolyte. The terephthalaldehyde derivative had the best physical properties of the dialdehydes; however, the ionic resistivities were comparatively high. Mechanical properties of film combinations treated with butyraldehyde and *p*-hydroxybenzaldehyde were inferior to those of the formaldehyde derivative; thus, there was little interest in further investigation of these materials. Although chemical inertness of polyvinyl formal - polyacrylic acid membranes to alkaline silver oxide has not been fully determined, it would be anticipated that such materials would probably degrade in this strong oxidizing environment. If this is true, then this class of separators would have more appropriate application in nickel-zinc and nickel-cadmium batteries than in silver-zinc cells.

The second membrane system studied comprised a conducting hydrophylic polymer suspended in an inert nonconducting support polymer. This separator can be considered a modification of the inorganic-organic separator which uses inorganic refractory materials such as zirconium dioxide and potassium titanate as filler materials. The use of a

polymeric filler is in response to the need for more flexible membranes. Greater separator flexibility is believed to be a requisite for long cycle life of batteries. A filler such as calcium polyacrylate, although insoluble in aqueous KOH, converts to a stiff gel when exposed to aqueous systems. The wet membrane may be portrayed as small isolated gel particles in a polymer matrix, whereas in the inorganic-organic Astropower separator, rigid crystals are held in the polymer body. A film with a stiff gel filler should have greater flexibility than one with a hard crystalline filler. Observations indicated this to be true for wet membranes. For dry films containing the unswelled polymer particles, this reasoning would not apply; thus, a dry film even with the polymeric filler would be as brittle as one with a crystalline filler. Of course, there are many support polymers besides PPO that may be used; however, because PPO is resistant to chemical oxidation by alkaline silver oxide, this material was used in this study. The calcium salt of polyacrylic acid was selected because it is insoluble in water; in addition, the selection of the calcium salt was influenced by the belief that calcium in the membrane would inhibit silver diffusion through the membrane (ref. 14); silver oxide possibly forms an insoluble calcium oxide - silver oxide ($\text{CaO-Ag}_2\text{O}$) species.

Similar membranes with a radiation-cross-linked polyacrylic acid filler were not as interesting as the CPA membranes. In general, the resistivity was higher and films were soft. The cross-linked material is difficult to powder by milling, whereas dry CPA is easily reduced to a fine powder.

There are other support and conducting polymer combinations as well as types of membranes that may be applicable to battery separator technology. However, at this point the data are insufficient to indicate how various combinations will perform. The purpose of this report was to present the concepts involved for two systems and the physical and electrical properties of these systems.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 26, 1977,
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TABLE I. - RESISTIVITY OF POLY (VINYL ACETAL) FILMS
FORMED BY TREATMENT OF POLYVINYL ALCOHOL
FILMS WITH VARIOUS ALDEHYDES

[Electrolyte: 45-percent KOH.]

Reagent	Treatment		Dry film thickness, μm	Resistivity, ohm-cm^2
	Time, min	Temperature, $^{\circ}\text{C}$		
None	---	-----	75	0.41
Formaldehyde	10	50-60	100 ↓	0.45
	5	60-70		.45
	30	50-60		1.0-4.0
	30	60-70		100-500
	120	75		>1000
Glutaraldehyde	30	60-70	~100	>1000
p-hydroxy-benzaldehyde	5	60-70	~100	~500

TABLE II. - RESISTIVITY OF POLYVINYL FORMAL -
POLYACRYLIC ACID FILMS AS FUNCTION OF
POLYVINYL ALCOHOL - POLYACRYLIC
ACID WEIGHT RATIO

[Treatment: formaldehyde reagent, 30 min at 60°
to 70°C ; electrolyte: 45-percent KOH.]

wt. polyvinyl alcohol wt. polyacrylic acid	Dry film thickness, μm	Resistivity, ohm-cm^2
100:0	60	~100
92:8	40	15
86:14	40	10
80:20	35	3.0
66:34	35	^a .48
56:44	35	.35

^aValue was 0.35 for film conditioned in hot (100°C) 45-percent KOH for 12 hr prior to test.

TABLE III. - RESISTIVITY OF MEMBRANES
COMPRISING POLYPHENYLENE OXIDE (PPO),
CALCIUM POLYACRYLATE (CPA),
AND 1,2-PROPANEDIOL (DIOL)

[Dry film thickness: 8 μ m; electrolyte: 45-
percent KOH.]

Parts by weight			Resistivity, ohm-cm ²	
PPO	CPA	Diol	R ₁ (a)	R ₂ (b)
27	10	3	3.4	----
40	20	3	4.3	3.4
27	20	6	.20	.20
27	20	0	2.3	.66
27	40	3	.15	----
27	20	3	.30	.30

^aFilm conditioned in 45-percent KOH
at room temperature for 12 hr.

^bFilm conditioned in 45-percent KOH
at 100° C for 12 hr.

TABLE IV. - RESISTIVITY OF MEMBRANES
COMPRISING POLYPHENYLENE OXIDE (PPO),
RADIATION-CROSS-LINKED POLYACRYLIC
ACID (PAA), AND 1,2-PROPANEDIOL (DIOL)

[Dry film thickness: 8 μ m; electrolyte: 45-
percent KOH.]

Parts by weight			Resistivity, ohm-cm ²	
PPO	PAA	Diol	R ₁ (a)	R ₂ (b)
40	10	3	5.6	3.6
27	10	3	4.7	2.8
27	10	6	1.0	1.0
20	10	3	1.4	1.2
27	20	3	.7	---

^aFilm conditioned in 45-percent KOH
at room temperature for 12 hr.

^bFilm conditioned in 45-percent KOH
at 100° C for 12 hr.



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